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Effects of High Pressure Nitrogen on the Thermal Stability of SiC Fibers

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ABSTRACT

Polymer-derived SiC fibers were exposed to nitrogen gas pressures of 7 and 50 atm at temperatures up to 1800 °C. The fiber weight loss, chemical composition, and tensile strength were then measured at room temperature in order to understand the effects of nitrogen exposure on fiber stability. High pressure nitrogen treatments limited weight loss to 3 percent or less for temperatures up to 1800 °C. The bulk Si-C-O chemical composition of the fiber remained relatively constant up to 1800 °C with only a slight increase in nitrogen content after treatment at 50 atm; however, fiber strength retention was significantly improved. To further understand the effects of the nitrogen atmosphere on the fiber stability, the results of previous high pressure argon treatments were compared to those of the high pressure nitrogen treatments. High pressure inert gas can temporarily maintain fiber strength by physically inhibiting the evolution of gaseous species which result from internal reactions. In addition to this physical effect, it would appear that high pressure nitrogen further improved fiber temperature capability by chemically reacting with the fiber surface, thereby reducing the rate of gas evolution. Subsequent low pressure argon treatments following the initial nitrogen treatments resulted in stronger fibers than after argon treatment alone, further supporting the chemical reaction mechanism and its beneficial effects on fiber strength.

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INTRODUCTION

As research in the field of ceramic matrix composites continues to expand, there is an increasing emphasis on the study and improvement of ceramic fibers for reinforcement of these materials. Adequate continuous reinforcement of a ceramic matrix composite requires small diameter fibers which are capable of maintaining high strength and high modulus at high temperatures. The polymer-derived SiC fibers which are commercially available possess many of the desired properties but are thermally unstable beyond 1200 °C.[1-3] These instabilities are believed to be caused by increased porosity and the growth of flaws which are initially produced during fiber fabrication. The mechanism for the flaw growth is reportedly due to internal reactions occurring between excess C and SiO_2 which are found in the as-produced fiber.[4] Grain growth, which is an inherent problem for the polycrystalline fiber, is also thought to be a cause of strength loss at temperatures beyond 1200 °C.[3,4]

The objective of this work was to determine the feasibility of maintaining fiber properties after exposure to high temperatures by applying high external nitrogen pressures while the fiber is heated. The initial phase of this work involved treatment of the as-received fibers in a high pressure inert argon atmosphere. The results of this work proved that high pressure argon was effective in delaying the chemical reactions which could lead to fiber degradation during composite processing, but was unable to sustain any long term stabilizing effect after pressure removal.[5] The present effort was aimed at not only maintaining properties during composite processing, but also retaining fiber properties after subsequent exposure to high temperatures at normal pressures during composite use. It was anticipated that the high pressure nitrogen treatment could not only physically inhibit the fiber

degrading chemical reactions, as was the case with high pressure argon, but also may chemically react with the fiber to form a more thermally stable material. In this paper, some of the pertinent data from the initial phase of the work will be presented and discussed in addition to the current results in order to explain the combined effects of the high pressure nitrogen treatments.

PROCEDURES

Materials

Ceramic grade Nicalon* SiC fibers were studied in this work. The fiber is formed from a polycarbosilane polymer precursor. Due to the air cure of the polymer during the fiber fabrication process, oxygen is introduced into the fiber composition. Thus the as-fabricated fiber is not stoichiometric SiC, but instead, is composed of a random network of SiC, SiO_2 and excess C. To facilitate handling of the fiber, a sizing is applied to the fiber during processing. This sizing is a nonuniform coating of polyvinyl acetate. It was not considered necessary to remove this sizing prior to heat-treatment since it decomposes below 1000 °C. The fibers are received in tow form with approximately 500 fibers per tow and an average diameter of 16 to 20 μm.

Heat-treatment

Fiber samples were treated in 7 and 50 atm N_2 (the upper pressure limit of the furnace) at temperatures ranging from 1200 to 1800 °C (Table I). Samples were placed in a clean tungsten cup covered with a loose lid and loaded in a tungsten lined resistance heated furnace. The tungsten which surrounds the sample within the furnace acts as a sensitive indicator of the

*Nippon Carbon Co., Tokyo Japan.

presence of oxygen at high temperatures. Since the tungsten showed no signs of oxidation from the high pressure nitrogen runs, it was assumed that there was little, if any, oxidation of the fibers themselves. Samples were held at temperature and pressure for 1 hr. To evaluate the long term effect of the N_2 treatments, fiber samples that were originally treated in 50 atm N_2 at 1200, 1400, and 1600 °C were placed in graphite crucibles and given a subsequent treatment in 1 atm argon for 1 hr at 1400 °C. This permitted comparison with fibers that had seen only a 1 hr treatment in 1 atm argon at 1400 °C or with fibers that had been initially heat treated in 1360 atm argon for 1 hr at either 1400 or 1600 °C followed by retreatment in 1 atm argon for 1 hr at 1400 °C (Table I).

Fiber Analysis

Fiber samples were weighed before and immediately after each heat-treatment to obtain weight loss measurements. Chemical analysis was performed on the as-received fibers and the heat-treated fibers to monitor C, O, and N levels. X-ray diffraction of crushed samples was used to qualitatively evaluate the extent of crystal growth of the microcrystalline beta SiC which is found in the as-received fiber and also to identify the phases which were present before and after heat-treatment. The heat-treated fibers were scanned both longitudinally and in cross-section in an electron microprobe in an effort to locate the position of the Si_3N_4 phase. Tensile strengths were obtained from testing single fibers. The tensile tests were performed at room temperature using a 25 mm (1 in.) gauge length and a constant crosshead speed of 1.3 mm/min (0.05 in./min). Approximately 10 fibers were tested to determine the average tensile strength for each condition. Microstructural changes in the fibers after the various heat-treatments were studied using a scanning electron microscope. The fibers which underwent a second

heat-treatment in 1 atm Ar at 1400 °C were subjected to the same property measurements as discussed above.

RESULTS AND DISCUSSION

Weight loss trends for the fibers treated in 7 and 50 atm N_2 are compared with those of the fibers treated in 1 and 1360 atm Ar in Fig. 1. The fibers treated in both 7 and 50 atm N_2 show little weight loss, approximately 3 percent, up to 1800 °C. The fibers treated in Ar displayed very different results. In atmospheric Ar, the fibers began to measurably lose weight at approximately 1200 °C, whereas, the high pressure Ar was able to delay fiber weight loss up to approximately 1600 °C. The fibers treated in atmospheric and high pressure argon both reached a maximum weight loss of approximately 28 to 30 percent when heated beyond 1600 and 1800 °C, respectively. Even though the N_2 pressure treatments were at much lower pressures than the Ar treatments, the weight loss of the N_2 treated samples was substantially less than that of the Ar treated fibers.

Table II presents results of the fiber bulk chemical analysis which are consistent with the weight loss results. The relative standard deviation for nitrogen was less than or equal to 6.9 wt % and that of oxygen and carbon was 5.0 wt % or less. Results in Table II reveal that the fibers treated in 50 atm N_2 retained fairly constant C and O levels up to approximately 1800 °C with only a small increase in bulk nitrogen content. Fibers which were treated in high pressure Ar maintained a relatively stable chemical composition up to approximately 1600 °C. After 1600 °C the fibers begin to lose both carbon and oxygen.

Weight loss trends and chemical analysis both indicate that treatment in overpressures of N_2 can more efficiently inhibit weight loss and shifts in chemical composition than treatment in a higher pressure inert gas, such as

argon. Since CO and SiO have been identified as the major vaporization species over Nicalon, with SiO predominating,[6] it is believed that SiO and CO may evolve according to the reactions[7]:

$$SiC + 2SiO_2 = 3SiO + CO \quad (1)$$

Above 1600 °C, the high pressure inert gas can no longer delay the evolution of SiO and CO from the fiber and the strength reducing reactions proceed freely.

When the fibers are heated in the presence of 50 atm N_2, thermodynamics predict Si_3N_4 to become more stable than SiC. With increased N_2 pressure SiC can be nitrided according to the equation:

$$3SiC + 2N_2 = 3C + Si_3N_4 \quad (2)$$

If SiO_2 is present in the system, then the formation of Si_3N_4 can proceed from the reaction:

$$SiC(s) + SiO_2(l) + 2/3\ N_2(g) = 1/3\ Si_3N_4(s) + SiO(g) + CO(g) \quad (3)$$

or

$$2SiC(s) + SiO_2(l) + 2N_2(g) = Si_3N_4(s) + 2CO(g) \quad (4)$$

if an excess of SiC is present.[8] Because of the over pressure of N_2, further decomposition or reaction of Si_3N_4 with SiO_2 is prevented. Cross-sections of the fibers were scanned for nitrogen by the electron microprobe. Because of the microprobe's large spot size and its limit of detectability for nitrogen, it was not possible to identify nitrogen in the bulk of the fiber. However, when the fiber surfaces were scanned longitudinally, a distinct peak for nitrogen was observed for the heat-treated fibers; thus indicating that Si_3N_4 formation occurs in a very thin region at the fiber surface. This thin layer may then be capable of limiting further internal reactions which cause fiber degradation by the evolution of oxygen-containing species.

The x-ray diffraction patterns in Figs. 2 and 3 display the crystallization behavior for the fibers treated in 1360 and 1 atm Ar and 50 and 7 atm N_2, respectively. The fibers which were treated in 1 atm Ar show distinct peaks for beta SiC forming as low as 1400 °C. At 1800 °C the sharpening of the beta SiC peaks is observed with only a slight formation of alpha SiC. With the increase of the Ar pressure to 1360 atm, the SiC peaks are less distinct at 1400 °C. At 1800 °C the major phase remains beta SiC. For the fibers treated in 7 atm N_2, only broad SiC peaks are observed. The fibers treated in 50 atm N_2 begin to show more distinct beta SiC peaks with heat treatment at 1800 °C. At this temperature, two prominent beta SiC peaks are apparent. The remaining peaks are due to crystallization of alpha Si_3N_4. The SiC peaks, in comparison to Si_3N_4, are still broad which indicates that the SiC is still very fine grained relative to the Si_3N_4.

In earlier work, crystal growth of the beta SiC structure of the Nicalon fiber was related to the fiber weight loss and accompanying shift in chemical composition.[5] It was found that as the fiber composition moved closer to stoichiometric SiC, rapid grain growth occurred. XRD results in Figs. 2 and 3 support this theory. The fibers treated in atmospheric and 1360 atm Ar lose large amounts of weight with treatment up to 1400 and 1800 °C, respectively; at these temperatures, the fibers also show a marked increase in crystal growth which is denoted by the narrowing of the peak widths. With treatment in N_2, the fibers never achieved over 3 percent weight loss up to 1800 °C. The wide peaks for SiC (Fig. 3), which reflect the microcrystalline grain structure which is present in the as-received fibers, can be correlated with the low weight loss and stable chemical compositions of the fibers treated in 7 and 50 atm N_2.

Room temperature tensile strength results for the Ar and N_2 treated fibers are plotted in Fig. 4. All of the fibers treated in N_2 showed improved strength properties over those of the Ar treated fibers. The nitrogen-treated fibers were able to maintain most of their as-received strength up to 1400 °C, after which the strength began to drop. The difference in the two nitrogen pressures used in this study produced only slight differences in strength. However, it should be noted that the difference in the two nitrogen pressures was much less than the difference between the two argon pressures which were used (due to limitations of the equipment). As expected, the fibers treated in atmospheric Ar display the lowest temperature for the onset of strength loss.

By comparing both weight loss and crystal growth tendencies with the tensile strengths of the treated fibers, it is evident that weight loss is more closely related to strength loss. With only a few percent weight loss, the fiber strength is reduced dramatically, whereas very little crystal growth is apparent at this point. This is particularly clear in the case of the fibers treated at 7 atm N_2. XRD traces show very little narrowing of the SiC peaks up to 1800 °C. But with only 3 percent weight loss at 1800 °C, the fibers have become too fragile to tensile test. Therefore, it is necessary to completely inhibit weight loss and the corresponding reactions in order to stop flaw growth and maintain fiber strength.

The micrographs in Figs. 5 to 8 display the differences in microstructures for the fibers treated in Ar and N_2 at 1600 and 1800 °C. At 1600 °C, visible coarsening of the microstructure is observed for only the fibers treated in atmospheric Ar (Figs. 5 and 6). At 1800 °C, both treatments in Ar have caused considerable coarsening of the microstructure throughout the fiber (Fig. 7). The fibers treated in N_2 at 1800 °C showed very little change

in the microstructure internally (Fig. 8). The difference between the microstructures of the N_2 and Ar treated fibers is presumed to be due to the formation of the Si_3N_4 phase at the surface of the fibers which were treated in N_2. Here again, the Si_3N_4, which is more stable in the N_2 atmosphere, appears to be able to limit further internal reactions thus maintaining a more stable fiber composition and microstructure. The surface of the fibers treated in 50 atm N_2 at 1800 °C, however, displayed excessive pitting. Pitting on the surface of these fibers is thought to be caused by the conditions under which the Si_3N_4 is formed. At 1800 °C, cavitation of the fiber surface may occur from rapid vaporization of Si. With the combination of the rapid loss of Si and the high N_2 pressure, the formation of a coarse Si_3N_4 product is favored.[9] Formation of a more uniform outer product is more likely with lower temperatures and higher pressures.

The combination of the effects of both increased gas pressure and chemical interaction are represented graphically in Fig. 9. Tensile strength is plotted versus increasing nitrogen and argon pressure for fibers treated at 1400 °C for 1 hr. Increased residual tensile strength is observed with higher pressure nitrogen treatments, similar to the argon results. However in addition to this pressure effect, the influence of the chemical interaction is apparent from both the improved strength retention at low pressures and the increased efficiency of the nitrogen gas. Only 50 atms nitrogen was necessary to retain a much higher strength than was possible with 1360 atm argon.

The effects of additional heat-treatments on the tensile strength of the pressure treated fibers are displayed in Fig. 10. The residual room temperature tensile strength of fibers treated in 1360 atm Ar or 50 atm N_2 at 1400 and 1600 °C for 1 hr are compared to the strengths of the same fibers after an additional 1 hr treatment in 1 atm Ar at 1400 °C. All of the fibers

lost strength after the second treatment. The fibers which were initially treated at 1400 °C in 50 atm N_2 were able to retain the highest strength, approximately 150 ksi. From the range of conditions studied in this work, these were considered the most favorable conditions for the formation of a uniform, protective Si_3N_4 layer. The retention of strength after the second treatment at 1400 °C in 1 atm Ar then becomes dependent on the ability to maintain the Si_3N_4 phase.

CONCLUSIONS

Thermal treatment of Nicalon fibers to 1600 °C in over pressures of N_2 has been found to be more effective in reducing weight loss, crystal growth, and strength loss than similar treatment in higher pressures of argon. A possible explanation for this behavior is that in the N_2 atmosphere, SiC is a less stable phase and a protective Si_3N_4 phase is formed on or near the surface of the fibers. It is thought that the Si_3N_4 phase may then seal off surface porosity and reduce further reactions within the fiber thus maintaining a microstructure which results in greater strength retention. In support of this chemical conversion effect, the N_2 treated fibers retreated in 1 atm argon were observed to be more thermally stable than as-received fibers treated in 1 atm argon only. However, full microstructural stability was not achieved, suggesting that the Si_3N_4 phase produced during these studies was not totally effective. Clearly further studies are needed to ascertain the potentially beneficial effects of even greater N_2 pressures and/or longer treatment times.

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TABLE I. - FIBER HEAT TREATMENT CONDITIONS

(a) Nitrogen treatments

Initial 1 hr treatments		Initial 1 hr treatment, 50 atm N_2, + °C	Additional 1 hr treatment, 1 atm Ar °C
7 atm N_2, °C	50 atm N_2, °C		
1200	1200	1200	1400
1400	1400	1400	1400
1600	1600	1600	1400
1800	1800	----	----

(b) Argon treatments

Initial 1 hr treatments		Initial 1 hr treatment, 1360 atm Ar, + °C	Additional 1 hr treatment, 1 atm Ar °C
1 atm Ar, °C	1360 atm Ar, °C		
1000	1000	----	----
1200	1200	----	----
1400	1400	1400	1400
1600	1600	1600	1400
1800	1800	----	----
2000	2000	----	----
2200	2200	----	----

TABLE II. - EFFECTS OF TEMPERATURE AND PRESSURE ON CHEMICAL COMPOSITION OF TREATED NICALON FIBERS

	Treatment	As-received	1400 °C	1600 °C	1800 °C
		Weight percent			
C	1360 atm Ar 50 atm N_2	30.1	26.7 32.4	31.7 30.9	23.4 30.0
O	1360 atm Ar 50 atm N_2	12.6	14.0 12.5	12.3 12.2	5.7 11.2
N	1360 atm Ar 50 atm N_2	None detected	None detected 0.081	0.1 .174	0.1 2.62

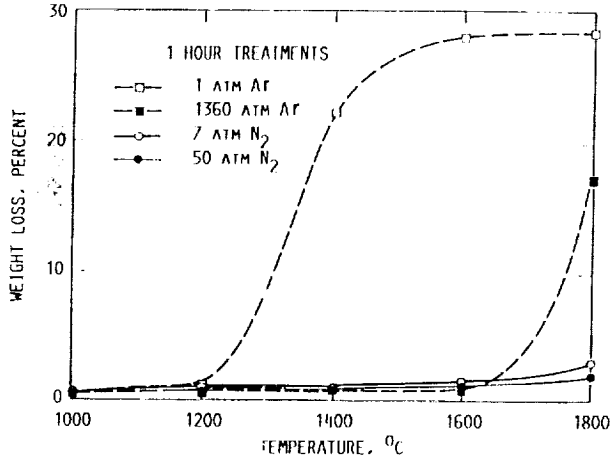


FIGURE 1. - EFFECTS OF TEMPERATURE AND PRESSURE ON THE WEIGHT LOSS OF TREATED NICALON FIBERS.

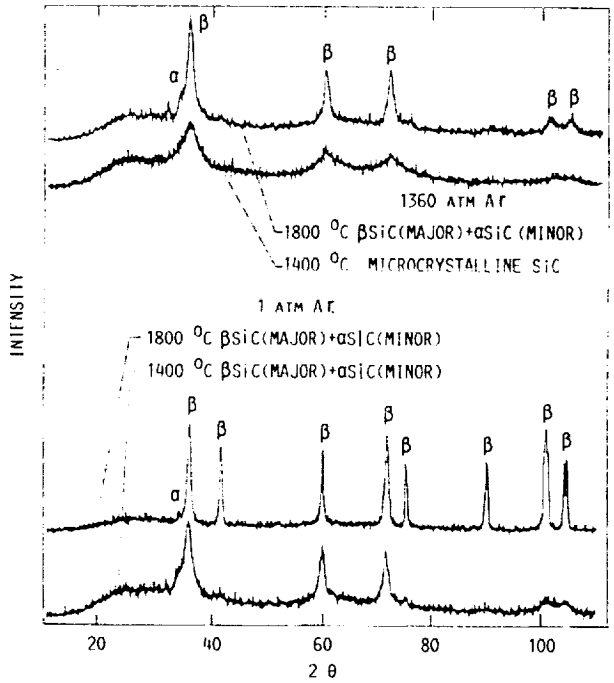


FIGURE 2. - EFFECTS OF TEMPERATURE AND PRESSURE ON THE X-RAY DIFFRACTION TRACES OF NICALON FIBERS TREATED IN ARGON.

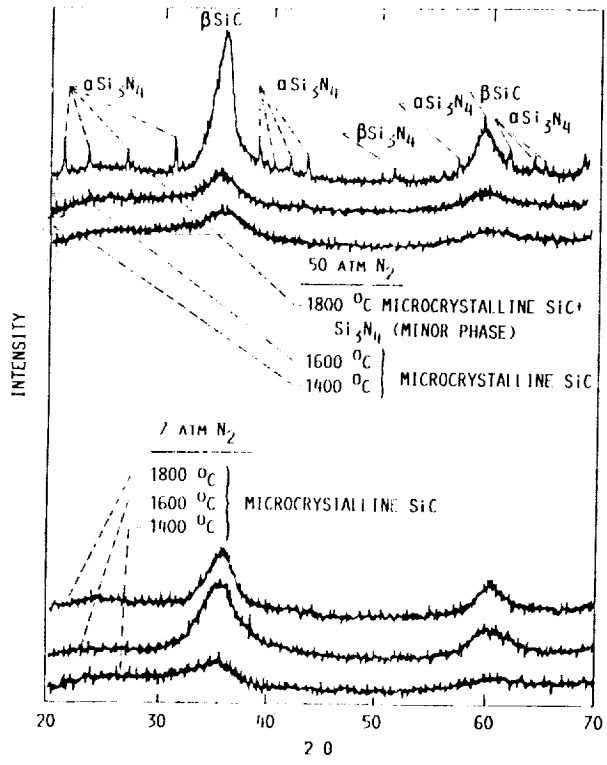


FIGURE 3. - EFFECTS OF TEMPERATURE AND PRESSURE ON THE X-RAY DIFFRACTION TRACES OF NICALON FIBERS TREATED IN NITROGEN.

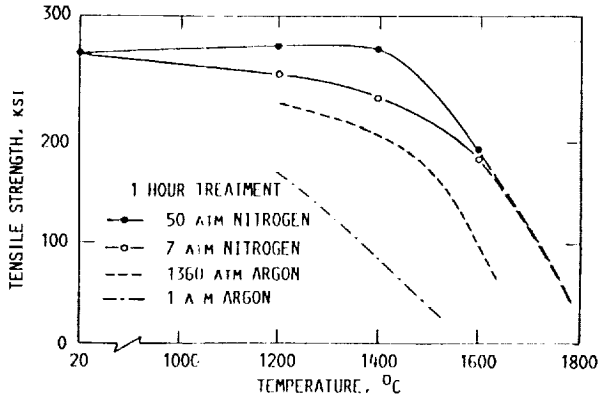
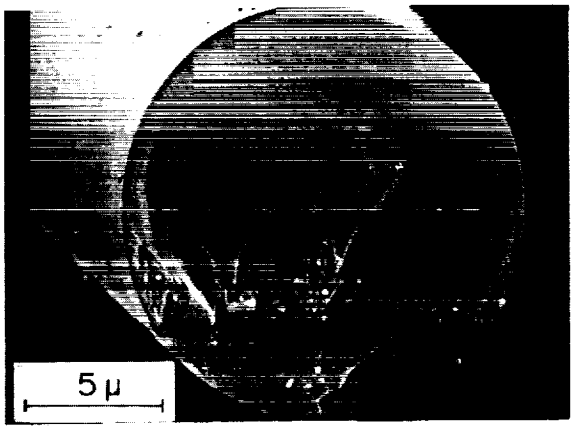
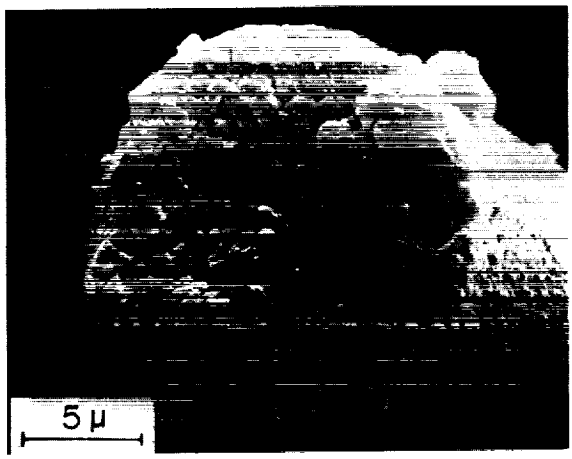


FIGURE 4. - EFFECTS OF TEMPERATURE AND PRESSURE ON THE TENSILE STRENGTH OF TREATED NICALON FIBERS.

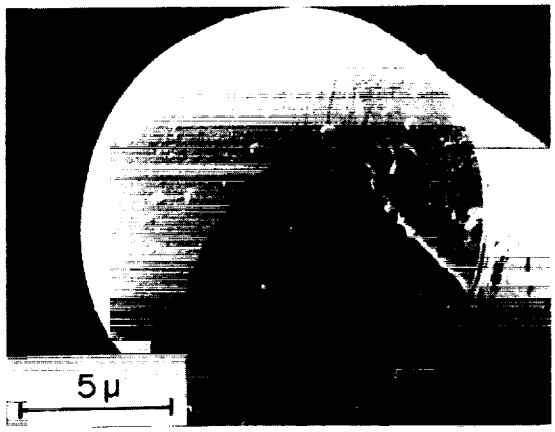


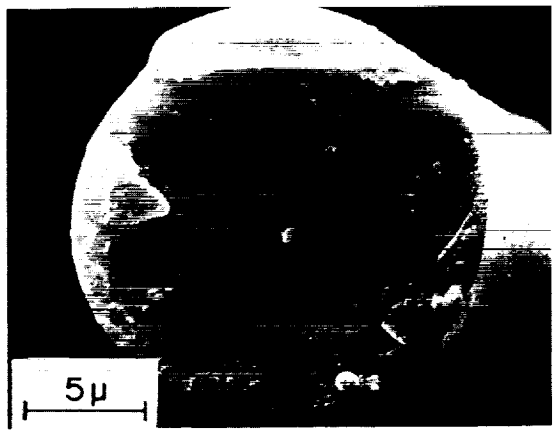
(a) 50 ATM, 1.3% WT LOSS, 194 KSI.



(b) 1 ATM, 28% WT LOSS.

FIGURE 5. - PHOTOMICROGRAPHS OF CERAMIC GRADE NICALON FIBERS HEATED TO 1600 ^{o}C IN ARGON.





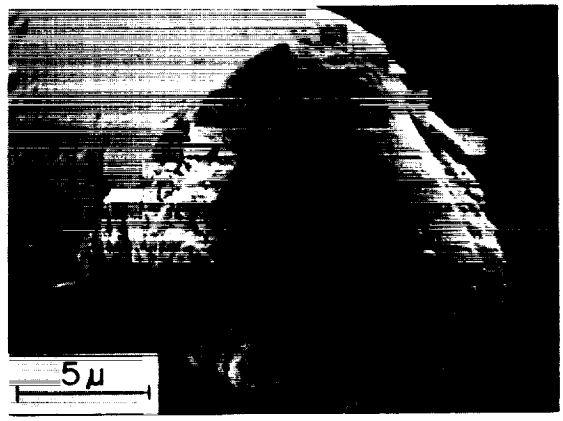
(b) 7 ATM, 1.3% WT LOSS, 188 KSI.

FIGURE 6. - PHOTOMICROGRAPHS OF CERAMIC GRADE NICALON FIBERS HEATED TO 1600 ^{o}C IN NITROGEN.

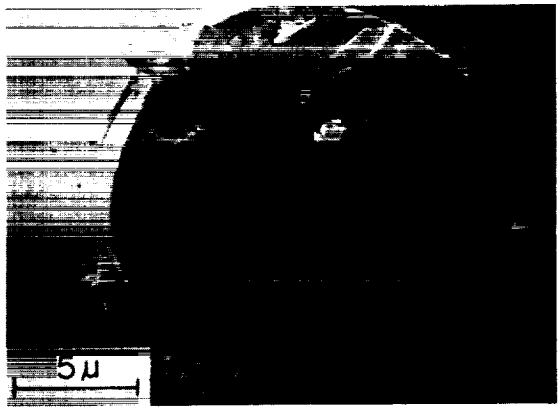
(a) 1360 ATM, 17.1% WT LOSS.

(b) 1 ATM, 28% WT LOSS.

FIGURE 7. - PHOTOMICROGRAPHS OF CERAMIC GRADE NICALON FIBERS HEATED TO 1800 ^{O}C IN ARGON.



(a) 50 ATM, 1.9% WT LOSS.



(b) 7 ATM, 3.0% WT LOSS.

FIGURE 8. - PHOTOMICROGRAPHS OF CERAMIC GRADE NICALON FIBERS HEATED TO 1800 ^{O}C IN NITROGEN.

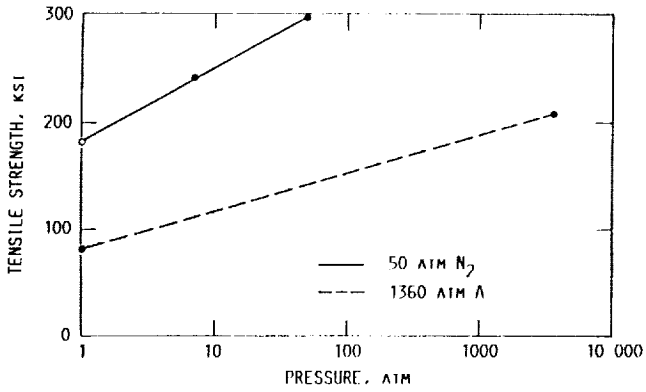


FIGURE 9. - EFFECTS OF PRESSURE ON TENSILE STRENGTH OF CERAMIC GRADE NICALON FIBERS HEAT-TREATED FOR 1 HOUR AT 1400 ^{o}C.

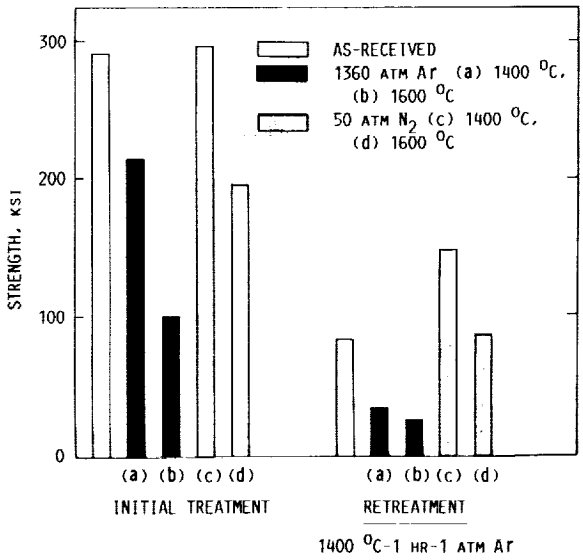


FIGURE 10. - RESULTS OF ADDITIONAL HEAT-TREATMENTS ON PRESSURE TREATED NICALON FIBERS.

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15. Supplementary Notes

16. Abstract

Polymer-derived SiC fibers were exposed to nitrogen gas pressures of 7 and 50 atm at temperatures up to 1800 °C. The fiber weight loss, chemical composition, and tensile strength were then measured at room temperature in order to understand the effects of nitrogen exposure on fiber stability. High pressure nitrogen treatments limited weight loss to 3 percent or less for temperatures up to 1800 °C. The bulk Si-C-O chemical composition of the fiber remained relatively constant up to 1800 °C with only a slight increase in nitrogen content after treatment at 50 atm; however, fiber strength retention was significantly improved. To further understand the effects of the nitrogen atmosphere on the fiber stability, the results of previous high pressure argon treatments were compared to those of the high pressure nitrogen treatments. High pressure inert gas can temporarily maintain fiber strength by physically inhibiting the evolution of gaseous species which result from internal reactions. In addition to this physical effect, it would appear that high pressure nitrogen further improved fiber temperature capability by chemically reacting with the fiber surface, thereby reducing the rate of gas evolution. Subsequent low pressure argon treatments following the initial nitrogen treatments resulted in stronger fibers than after argon treatment alone, further supporting the chemical reaction mechanism and its beneficial effects on fiber strength.

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